

RESIDUE REMOVERS FOR ELECTROHYDRODYNAMIC CLEANING OF SEMICONDUCTORS

[0001] The application claims priority to Provisional App. No. 60/455,439 filed March 18, 2003, the disclosure of which is incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates in general to a method and apparatus for cleaning surfaces of substrates, and in particular to the removal of organic films, particulate matter and other contaminants from the surface of semiconductor wafers, by impacting the surface with droplets comprising an oxidizer. In another aspect the invention relates to a method of modifying said substrate surface by depositing a modifying agent, for example an organometallic agent capable of reacting to leave a metal atom, by impacting the surface with droplets comprising organometallic compounds.

BACKGROUND OF THE INVENTION

[0003] The removal of contaminants from surfaces is critical for the profitable manufacturing and subsequent performance of many devices and processes. For example, device yields in semiconductor fabrication facilities are adversely affected by defects caused by particulates adhering to wafer surfaces. More than 80% of the yield loss of volume- manufactured VLSI's is attributed to particulate microcontamination. As device geometries continue to shrink and wafer sizes increase, particle contamination will have an ever increasing impact on device yields. New technologies will be required to clean wafer surfaces to meet national goals for producing 0.07 micron feature sizes by the year 2010. The requirements for finer polishing are leading to smaller abrasive particles. It is now recognized that the future need in semiconductor wafer processing requires removal of particulates 0.1 micron in size and smaller which are highly resistant to removal by conventional cleaning technologies. Present particle removal technologies become increasingly ineffective as "killer" particle size decreases.

[0004] Particles generated within process tool equipment, especially in the backend of a multilevel process, represent a major source of yield loss in terms of defective chips. At the present time, there is no commercially available, in-situ cleaning instrumentation for processing wafers in vacuum. The requirements placed on surface cleanliness for microelectronics device fabrication also apply to the

manufacturing of micromachines and microsensors based on silicon or gallium arsenide wafer preparation technology.

[0005] In addition to cleaning semiconductor wafers and processing tools, the present invention also relates to the cleaning of ground or spacecraft optics such as mirrors, lenses and windows. Other areas of application of the invention include the cleaning of silicon or other substrate materials to lower costs and uphold reliability during the manufacturing of flat panel displays; cleaning spacecraft thermal control surfaces and solar panels; cleaning surfaces in preparedness for deposition of thick or thin film materials to improve adhesion or growth dynamics; precision cleaning and removal of contaminants from vacuum chamber walls and internal mechanical/optical systems in major facilities such as the National Ignition Facility for fusion research and surfaces critical for the control of pharmacological cross- contamination.

[0006] Additional areas of application for the present invention include the cleaning of critical surfaces relevant to computers such as magnetic disk storage media. The continued evolution of computer technology has resulted in increasing demands for chemically clean and particulate-free surfaces. As computer technology continues to rely on microelectronics devices that shrink in size, product yield has become increasingly vulnerable to chemical and particulate contaminants.

[0007] Thin film structures are used in a variety of industrial applications including optical components, industrial platings, solar cells, wear and corrosion resistant coatings and coatings for transmissive and reflective elements to name a few. Thin films structures are adversely affected by the presence of chemical and micron- sized contaminants which impede the growth, adhesion, wear resistance and stability of the films. The present invention provides an enhanced cleaning process for a variety of solid surfaces compared to conventional cleaning techniques used in the above applications. For a review of cleaning techniques for removing particulates from surfaces, see J. Bardina, "Methods For Surface Particle Removal: A Comparative Study", Particulate Sci.Technol., 6, 121, 1988.

[0008] At present there are two principal methods of cleaning wafer surfaces: liquid phase or "wet" cleaning and gas phase or "dry" cleaning designed to remove process chemicals, films and particulate contamination. These methodologies suffer from several drawbacks, the most serious being that no single technology rids surfaces of organic films, trace metallic elements or particulates simultaneously. In some cases, the cleaning process is a source of contaminants itself. Even megasonic techniques, which can remove particulates in a given size range may not be effective for removing particulates of about 0.1 micron or less. Furthermore, ultrasonic cleaning efficiencies show some dependency on particulate composition and morphology. Wet cleaning technologies also suffer

by consuming large quantities of water. The need to conserve water and reduce costs associated with water usage are obvious. Additionally, wet cleaning technologies consume large quantities of environmentally hazardous chemicals such as inorganic acids, bases and etches including sulfuric acid, phosphoric acid, hydrofluoric and hydrochloric acids; ammonium fluoride; ammonium, sodium and potassium hydroxides and hydrogen peroxide to mention a few. These materials create proper handling and waste storage problems. The current status of wet chemistry cleaning technologies is discussed by Hattori, "Trends in Wafer Cleaning Technology", Solid State Technol. Suppl., p.S7, May, 1995.

[0009] The use of dry ice snow flakes, formed by the expansion of liquid CO₂ jet sprays, have also been used to clean spacecraft optical surfaces and semiconductor devices. These applications are discussed in M. M. Hills, "Carbon Dioxide Jet Spray Cleaning of Molecular Contaminants", J.Vac.Sci.Technol. A13(1), 30, January/February 1995 and R. Sherman et al. , "Dry Surface Cleaning Using CO₂ Snow", J.Vac.Sci. Technol.,B9(4), 1970, July/August 1991. Although capable of removing organic films and particulates, CO₂jet sprays are ineffectual for removing submicron particulates (< 0.1 micron) to levels specified for future microcontamination-free manufacturing of wafers.

[0010] Other "dry" cleaning technologies for removing contaminants from semiconductor wafers include gas-phase cleaning which uses reactive gaseous radicals formed by the excitation of process gases. These processes suffer from the use of complex chemistries which can result in damaged surfaces or removal of substrate material when attempting to remove particulate contaminants.

[0011] United States patent Nos. 4,896,035 and 4,835,383 disclose an ion detection system and method for detection of low or high mass ions. United States patent No. 4,762,975 discloses a method for producing ultrafine particles. United States patent No. 4,462,806 discloses a method for purifying metals and semiconductors. United States patent No. 4,318,028 discloses production of an ion beam. United States patent No. 4,264,641 discloses electrohydrodynamic production of particulates. United States patent No. 4,124,801 discloses a method for separating materials, such as isotopes. United States patent Nos. 3,893,131 and 3,848,258 disclose an ink drop printer. The foregoing patents are incorporated herein by reference in their entireties.

SUMMARY OF THE INVENTION

[0012] One aspect of the present invention relates to a method of cleaning or modifying a surface. In one embodiment, the method includes (a) introducing a first liquid to a first cluster generation site, the first liquid comprising an oxidizing agent; (b) subjecting the first liquid to electrical forces

higher than a surface tension of the first liquid to prepare a first plurality of clusters, wherein the clusters are formed from the first liquid; and (c) impacting clusters of the first plurality of clusters upon a first portion of the surface. In step (c), the phrase “clusters of the first plurality of clusters” means at least a portion of the first plurality of clusters. Advantageously, the clusters are less than a micron in diameter.

[0013] The oxidizing agent may comprise a hydroxylamine compound, e.g., at least one of hydroxylamine, an (organic) derivative of hydroxylamine, a salt of hydroxylamine, and a salt of a derivative of hydroxylamine. In a preferred embodiment, the first liquid comprises at least one solvent, such as water and/or a poly-alcohol, and at least one of hydroxylamine, a derivative of hydroxylamine, a salt of hydroxylamine, and a salt of a derivative of hydroxylamine. Preferred hydroxylamine compounds are hydroxylamine, an N-substituted hydroxylamine (N-H,R,OH) or an N,N-substituted hydroxylamine (N-R,R,OH) wherein the R is a C₁ to C₄ alkyl, a carboxyl, or combination thereof.

[0014] Relative to the weight of the first liquid, the total weight of the at least one of hydroxylamine, a derivative of hydroxylamine, a salt of hydroxylamine, and a salt of a derivative of hydroxylamine is at least 25 percent. For example, the total weight of the hydroxylamine, a derivative of hydroxylamine, a salt of hydroxylamine, and a salt of a derivative of hydroxylamine may be at least 0.25 grams, at least 0.30 grams, or at least 0.35 grams per gram of the first liquid. The bulk of the liquid may consist essentially of at least one solvent. Alternatively, the bulk of the liquid may comprise at least one solvent and other compounds, such as at least one of at least one corrosion inhibitor, at least one chelating agent, and optionally at least one metallic compound. In a preferred embodiment, the oxidizing agent comprises at least one of hydroxylamine and a derivative of hydroxylamine and the total weight thereof is at least 25 percent relative to the weight of the liquid. For example, the total weight of the at least one of hydroxylamine and a derivative of hydroxylamine may be at least 0.25 grams, at least 0.30 grams, or at least 0.35 grams per gram of the first liquid. The bulk of the liquid may consist essentially of at least one solvent. Alternatively, the bulk of the liquid may comprise at least one solvent and other compounds, such as at least one of at least one corrosion inhibitor, at least one chelating agent, and at least one metallic compound.

[0015] In one embodiment, the first liquid consists essentially of at least one hydroxylamine compound, and optionally but preferably, an amount of solvent sufficient to form a stable composition. As is known in the art, some forms of hydroxylamine must be aqueous or dissolved in a polar solvent. For example, pure hydroxylamine is unstable unless diluted with at least about 50% water (or less preferably with other solvents). Salts of hydroxylamine can be more concentrated or

even be obtained and used in pure form, as can many organic hydroxylamine derivatives. In a preferred embodiment, the hydroxylamine is dissolved in sufficient solvent, e.g., water, preferably very high purity water, so that the composition is stable. One embodiment of the first liquid consists essentially of aqueous hydroxylamine. One preferred embodiment of the first liquid consists essentially of aqueous hydroxylamine, where the concentration of hydroxylamine is between 5% and 50% by weight.

[0016] In another embodiment, the first liquid may consist essentially of a hydroxylamine compound and a solvent. The solvent preferably comprises at least two of water, an alkanolamine, an amide, a glycol, or dimethylsulfoxide. One preferred group is monoalkanolamines. The solvent may comprise an organic compound having at least one hydroxyl group. For example, the solvent may comprise an organic compound having fewer than 20 carbon atoms and at least two hydroxyl groups.

[0017] In another embodiment, the first liquid having a hydroxylamine compound and a solvent may additionally comprise an acid. The acid may comprise, for example, at least one of nitric acid, acetic acid, sulfuric acid, peroxymonosulfuric acid, perchloric acid, peracetic acid, perchromic acid, periodic acid, perchloric acid, perbromic acid, perfluoric acid, and perboric acid. Preferred inorganic acids are nitric acid and phosphoric acid. Preferred organic acids include acetic acid, glycolic acid, maleic acid, malonic acid, oxalic acid, and gallic acid. Ascorbic acid or citric acid can be added. Generally, the mineral acid is present in an amount between 0.1% and 5% by weight. The organic acid, if present, can be added in an amount between 0.5% and 10%, for example.

[0018] In another embodiment, the first liquid comprises in addition to the hydroxylamine compound at least one corrosion inhibitor. The corrosion inhibitor may comprise, for example, at least one of benzotriazole and a derivative of benzotriazole. Alternatively, the corrosion inhibitor may comprise a dihydroxybenzene or a trihydroxybenzene, optionally substituted with one C₁ to C₄ alkyl moiety. As little as 1% can be useful. The total weight of the at least one corrosion inhibitor may be at least 5 percent, at least 15 percent, or at least 25 percent, relative to the weight of the first liquid. For example, the total weight of the at least one corrosion inhibitor may be at least 0.05 grams, at least 0.15 grams, or at least 0.25 grams per gram of the first liquid.

[0019] Preferred first liquids comprise a hydroxylamine, water, and an alkanolamine or aminoethoxyethanolamine.

[0020] In another embodiment, the first liquid may comprise periodic acid in an amount between 0.2% and 5%. Such a composition is preferably substantially free of hydroxyamine

[0021] In an alternative embodiment, the oxidizing agent may be hydroxylamine-free and comprise at least one oxidizing agent having at least one peroxy group. For example, the oxidizing agent having at least one peroxy group may comprise at least one of hydrogen peroxide, urea hydrogen peroxide, a monopersulfate, a dipersulfate, peracetic acid, a percarbonate, and an organic peroxide. The total weight of the at least one oxidizing agent having at least one peroxy group may be at least 15 percent, at least 25 percent, or at least 35 percent, relative to the weight of the first liquid. For example, the total weight of the at least one oxidizing agent having at least one peroxy group may be at least 0.15 grams, at least 0.25 grams, or at least 0.35 grams per gram of the first liquid. This liquid may comprise polar organic solvents, water, acids, and corrosion inhibitors.

[0022] In another embodiment, the first liquid comprises at least one corrosion inhibitor. The corrosion inhibitor may comprise, for example, at least one of benzotriazole and a derivative of benzotriazole. The total weight of the at least one corrosion inhibitor may be at least 5 percent, at least 15 percent, or at least 25 percent, relative to the weight of the first liquid. For example, the total weight of the at least one corrosion inhibitor may be at least 0.05 grams, at least 0.15 grams, or at least 0.25 grams per gram of the first liquid.

[0023] In another embodiment, the method comprises the further steps of (d) introducing a second liquid to a second cluster generation site, the second liquid comprising a corrosion inhibitor; (e) subjecting the second liquid to electrical forces higher than a surface tension of the second liquid to prepare a second plurality of clusters; and (f) impacting clusters of the second plurality clusters upon a second portion of the surface. The corrosion inhibitor preferably comprises benzotriazole or a derivative of benzotriazole. The corrosion inhibitor may alternatively comprise a dihydroxybenzene or trihydroxybenzene compound. The first and second cluster generation sites may be the same. Such second liquid can be used to apply a blanket or a small amount of corrosion inhibitor on the surface.

[0024] The step of (c) impacting may comprise impacting the surface with clusters having a first average kinetic energy and the step of (f) impacting comprises impacting the surface with clusters having a second, smaller average kinetic energy. For example, the step of (f) impacting may comprise impacting the surface with clusters having an average kinetic energy at least 15 percent less, at least 25 percent less, or at least 35 percent less, than an average kinetic energy of the first plurality of clusters.

[0025] In a preferred embodiment, the cluster generation site comprises an opening through which liquid is introduced to the cluster generation site. The liquid exiting the opening and the surface to be impacted with clusters may be subjected to an electrical potential difference therebetween.

During the step of (f) impacting, the absolute potential difference may be at least 15 percent less, at least 25 percent less, or at least 35 percent less, than during the step of (c) impacting.

[0026] At least a portion of the second portion of the surface may be subjected to the steps of (f) impacting and (c) impacting. The step of (f) impacting may be performed after initiating the step of (c) impacting.

[0027] In one embodiment, at least a portion of the first portion of the surface is not subjected to the step of (f) impacting.

[0028] For at least a portion of the second portion of the surface also subjected to the step of (c) impacting, the step of (f) impacting may be performed for a total time T . For at least a time $0.8 \times T$, the step of (f) impacting may be performed without also performing the step of (c) impacting. For example, for a particular portion of the surface, the step of (c) impacting may be initiated at a time t_0 and carried out for 30 seconds. For the same portion of the surface, the step of (f) impacting may be carried out for 100 seconds. Preferably, the step of (f) impacting is performed for at least 80 seconds without concurrently performing the step of (c) impacting. The step of (f) impacting may be performed after initiating the step of (c) impacting. The step of (f) impacting may be performed after completing the step of (c) impacting.

[0029] In one embodiment, the steps of (c) impacting and (f) impacting are performed while subjecting the first and second portions of the surface to a gas pressure of less than 500 torr. Preferably, once one of the steps of (c) impacting and (f) impacting has been initiated, the first and second portions of the surface are not subjected to a gas pressure of greater than 500 torr until at least after the other of the steps of (c) impacting and (f) impacting has also been initiated.

[0030] At least one of the first and second liquids may be essentially free of metals.

[0031] In one embodiment, the method comprises the steps of: (g) depositing at least one organometallic compound upon a second portion of the surface; and (h) annealing the at least one organometallic compound to thereby provide the second portion of the surface with a metallic coating. The step of (g) depositing may comprise: (i) introducing a third liquid to a third cluster generation site, the third liquid comprising the at least one organometallic compound; (j) subjecting the third liquid to electrical forces higher than a surface tension of the third liquid to prepare a third plurality of clusters; and (k) impacting clusters of the third plurality clusters upon a third portion of the surface. The first and third cluster generation sites may be the same.

[0032] The step of (g) depositing may comprise depositing at least two different metals upon the second portion of the surface. The metallic coating may be annealed to provide at least one alloy.

[0033] The steps of (c) impacting and (k) impacting may be performed while subjecting the first and third portions of the surface to a gas pressure of less than 500 torr. Preferably, once one of the steps of (c) impacting and (k) impacting has been initiated, the first and second portions of the surface are not subjected to a gas pressure of greater than 500 torr until at least after the other of the steps of (c) impacting and (k) impacting has also been initiated.

[0034] In one embodiment, for at least $1 \times 10^{-5} \text{ cm}^2$ of the third portion of the surface, the step of (g) depositing comprises depositing at least about $9 \times 10^{-8} \text{ g/cm}^3$ of metal, for example, at least about $100 \times 10^{-8} \text{ g/cm}^3$ of metal per square centimeter.

[0035] Another aspect of the invention relates to a method for modifying a surface. In one embodiment, the method comprises (a) introducing a first liquid to a first cluster generation site, the first liquid comprising a reducing agent; (b) subjecting the first liquid to electrical forces higher than a surface tension of said liquid to prepare a first plurality of clusters; and (c) impacting clusters of the first plurality of clusters upon a first portion of the surface.

[0036] The reducing agent may comprise at least one of hydrazine and a derivative of hydrazine. In one embodiment, the total weight of the at least one of hydrazine and a derivative of hydrazine is at least 5 percent, at least 10 percent, or at least 20 percent relative to the weight of the first liquid. For example, the total weight of the at least one of hydrazine and a derivative of hydrazine may be at least 0.05 grams, at least 0.10 grams, or at least 0.20 grams per gram of the first liquid.

[0037] Another aspect of the invention relates to a method for modifying a surface. In one embodiment, the method comprises (a) introducing a first liquid to a first cluster generation site, the first liquid comprising an organometallic compound; (b) subjecting the first liquid to electrical forces higher than a surface tension of the first liquid to prepare a first plurality of clusters; and (c) impacting clusters of the first plurality of clusters upon the surface, wherein at least some of the organometallic compound deposits upon the surface.

[0038] The method may further comprise (d) subjecting the surface deposited organometallic compound to annealing whereby an at least partial metallic coating is formed upon the surface. The step of annealing may comprise heating the surface. The step of annealing may comprise exposing the surface to at least one gas, for example, ammonia, nitrogen, oxygen, a halogen, and an inert gas, e.g., at least one of helium and argon.

[0039] At least two different metals may be deposited upon the surface, wherein subjecting the surface to annealing comprises formation of a metallic alloy upon the surface.

[0040] During the step of impacting the surface with clusters prepared from a liquid comprising an organometallic, at least a portion of the surface may be subjected to an electrical charge whereby the

clusters impacting upon the surface are either attracted to or repelled from the charged portion of the surface. For example, a conductive portion of the surface, such as a metallic portion, may be subjected to a charge having an opposite polarity with respect to a charge upon the clusters whereby clusters are attracted to the charged portion of the surface and preferentially impact thereupon as compared to other portions of the surface. In this embodiment, the average kinetic energy of the clusters may be less than 500 MeV, for example less than 200 MeV, for example less than 50 MeV.

[0041] In one embodiment, a plurality of clusters having a negative charge are prepared. Electrons are injected into the plurality of clusters, whereby the clusters acquire an additional negative charge before impacting upon the surface. The additional negative charge causes disruption of the clusters whereby the size of the clusters is further reduced.

[0042] Formation of clusters, such as beams of high energy clusters, preferably comprises introducing a liquid to a cluster generation site, which may comprise an opening of a passage, such as an opening of a capillary. The opening by which liquid is introduced to the cluster generation site may have any suitable shape, such as round, elliptical or slit-like. More than one opening may be provided.

[0043] By applying an electric field to the cluster generation site, for example to the tip of a capillary or to the edges of a slit, the fluid, which is preferably conductive, is electrostatically atomized providing a plurality of clusters, which are preferably charged upon formation. The electrical field for atomization, which may be of the order 10^5 volts/cm or greater, may be established by applying a potential difference between, for example, the opening of the capillary and a counterelectrode or extractor.

[0044] The charged clusters are electrostatically accelerated by the extraction field to hypervelocities and directed toward a target substrate (e.g., wafer). Because the clusters may be multiply charged upon formation, acceleration through 10 kV or more results in impact energies greater than 0.5 million electron volts. Because of their massive size compared to the ions of ion beams, clusters expend their energy over an extended area of the target causing simultaneous liftoff and removal of particulates having micron and submicron dimensions, organic films and metallic contaminants. Although individual cluster impact energies are high, the energy is shared by the large number of cluster nucleons. This results in specific energies at impact less than 1 eV/nucleon, well below material sputtering thresholds, preventing direct etching or damage to impacted surfaces during the contaminant removal process. Dislodged contaminants may be collected by, for example, using a cryogenic shroud thereby preventing their re- introduction on cleansed surfaces. Substrate

charging may be prevented by introducing electrons into the plurality of clusters, which electrons neutralize the charge on the clusters.

[0045] To increase the area of the target cleansed and decrease the time required to remove contaminant species, a plurality of capillary emitters may be configured into two or more arrays preferably disposed adjacent and parallel to each other. To prevent target substrate charging, charged clusters emitted from single capillary emitters or multiple arrays are neutralized by ejecting electrons into the beam. A novel means for cluster beam neutralization uses two arrays; one array operated with positive high voltage to generate positive clusters and the other operated at negative high voltage to form negative clusters. The array voltages are adjusted independently until the net charge buildup on a target substrate is approximately zero.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] The present invention is discussed below in reference to the drawings in which:

[0047] FIG. 1 is a diagram showing the basic concept and apparatus for producing charged clusters used to clean or remove contaminants from surfaces such as semiconductor wafers in accordance with the present invention.

[0048] FIG. 2 shows a capillary emitter for generating a charged cluster beam subsequently neutralized by injecting electrons into the beam.

[0049] FIG. 3 is a partial perspective view showing a plurality or array of capillary emitters in combination with a thermionic electron emitting filament for beam neutralization.

[0050] FIG. 4 is a perspective view showing a bipolar arrangement consisting of alternating arrays of positive and negative capillary emitters for beam neutralization.

[0051] FIG. 5 is a perspective view showing a linear slit capillary emitter geometry for generating a charged cluster beam.

[0052] FIG. 6 is a perspective view of a capillary cluster emitter with associated ion optics for focusing and electrostatic deflection for positioning the cluster beam at designated target areas.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0053] One aspect of the present invention relates to an apparatus and method for modifying a surface, such as to remove surface contaminants and/or to deposit compounds upon the surface. The surface may include, for example, a semiconductor or data storage medium, for example, a magnetically or optically readable storage medium, e.g., a computer hard drive. The surface may

comprise a surface have microfabricated surface features, such as a chemical analysis device having surface features with dimensions of less than about 10 microns.

[0054] Methods of the invention preferably comprise subjecting a liquid to electrical forces sufficient to prepare a plurality of clusters or microdroplets, which terms are used interchangeably herein. The clusters comprise material present in the liquid when subjected to the electrical forces. For example, the clusters may comprise solvent and, if present, solutes present in the liquid. As discussed further below, the clusters preferably have an average diameter smaller than 10 microns, for example, less than 0.5 micron, such as less than 0.1 micron. The clusters may have average diameters of at least 0.001 microns, for example at least 0.005 micron.

[0055] The electrical forces preferably exceed a surface tension of the liquid by an amount sufficient to disrupt droplets of the liquid whereby clusters are formed. The clusters may also be subjected to electrical forces that accelerate the clusters toward a surface to be impacted with the clusters. The electrical forces that prepare the clusters may be the same electrical forces that accelerate the clusters. The electrical forces may be electrostatic or time varying.

[0056] Referring to FIGS. 1 and 2, a device for modifying a surface comprises an emitter 32 configured to form a plurality 34 of micron or submicron sized clusters. By way of a non-limiting example, the emitter 32 can have the form of a capillary having a bore 31 with a diameter of 0.0025 to 0.01 cm. An emitter tip 33 seen in FIG. 2, according to a particularly preferred geometry, tapers at an angle between 20-45°. Although this emitter tip is preferred, satisfactory operation can be obtained with emitters having different end configurations, such as a blunt end. It is fully contemplated within the scope and spirit of the invention that other emitter geometries are possible that will provide clusters having suitable characteristics. The actual dimensions of the capillary bore 31 will depend on the desired flow rate and physical properties of a fluid 21 introduced to the emitter.

[0057] In a preferred embodiment, the outside diameter 39 of the emitter may be, for example, from 0.02 to 0.08 cm, although larger or smaller dimensions may be suitable. The emitter may be formed from many materials including materials which are electrically conductive or insulating. Conductive materials include but are not limited to stainless steel and platinum. Platinum is the preferred material since it exhibits excellent resistance to electrochemical corrosion thereby increasing the lifetime of the emitter 33. Electrically insulating materials include but are not limited to polymers, glass, ceramics and fused silica.

[0058] In a preferred embodiment of the present invention, a fluid 21, which is preferably conductive, such as a conductive liquid, flows from a reservoir 18 through a fluid conduit 20 to the

emitter 32. A two-way shutoff valve (V4) 15 may be inserted in the fluid conduit between the reservoir and capillary emitter as a means of terminating or restarting the flow of fluid to the emitter. Preferred fluid flow rates for a single capillary tube emitter 32 are from 0.1 to 3 microliters/minute although flow rates outside this range may be used. Fluid flow rates may be determined by any combination of the geometric flow impedance of the emitter 32; by the pressure above the fluid in the reservoir 18; and by the fluid temperature.

[0059] The liquid introduced to the emitter may have a temperature of less than a boiling point of the liquid. In one embodiment, the liquid introduced to the emitter has a temperature of less than about 200 °C, of less than about 150 °C, of less than about 100 °C, or of less than about 75 °C.

[0060] The pressure above the fluid in the reservoir may be regulated by a pressure/vacuum controller 16 which automatically opens and closes a combination of on-off solenoid valves (V1,V2,V3) 14. With valve (V2) closed, opening valve V(1) connects a regulated gas supply 12 and a gas conduit 13 to the reservoir 18 when valve (V3) is open, exposing the fluid to a positive pressure applied by gas supply 12. When valve (V1) is closed, opening valve (V2) connects a vacuum pump 10 to the reservoir 18 when valve (V3) is open, reducing the pressure over the fluid in reservoir 18. In this manner, reservoir pressures can be adjusted, but not limited to, a preferred range of 50 torr to 1500 torr for controlling flow rates to the emitter. An inert gas such as helium or argon is preferred for pressurizing the reservoir 18 containing the fluid 21. In general it is recommended that the pressurizing gas used resist solvation by the fluid thereby reducing the risk of bubble formation in the fluid conduit 20. The fluid 21 may be degassed before loading in the reservoir 18 to reduced to reduce the concentration of dissolved gasses.

[0061] Flow rates can also be controlled by heating the fluid 21, particularly for fluids whose viscosities show large variations with changes in temperature. An example of a fluid exhibiting this property is one consisting of high concentrations of glycerol or other poly-alcohol. Although various conventional means for heating the solution are available, a satisfactory method is illustrated in FIG. 1. The fluid conduit 20 is vacuum sealed and passes through a vacuum flange 24. The vacuum flange in turn is mounted and sealed to a high vacuum chamber 27. A heater 26, preferably a flexible, silicone rubber heater encloses and is attached to the flange 24. Heat conducted through the flange 24 warms the fluid conduit 20 in intimate contact with the flange. A thermocouple 22 senses the flange temperature which is regulated by a temperature controller 24. Suitable flange temperatures for controlling the flow rates of glycerol fluids range from ambient to 60° C.

[0062] A preferred liquid used for cluster formation in the present invention comprises a solvent, preferably high purity solvent, and, optionally a solute. It should be understood, however, that a

solvent is not required. Preferred solvents have gas phase dipole moments of at least 1.5 debye, for example, at least 1.70 debye, or at least 1.85 debye. The solvent may have a dielectric constant of at least 40, for example, at least 70, such as at least 80. Examples of preferred solvents include water and organic solvents including alcohols, poly-alcohols, amines, formamides, ketones, aldehydes, nitriles, and sulfoxides.

[0063] Preferred alcohols have fewer than 30 carbon atoms, such as fewer than 10 carbon atoms. Examples of preferred alcohols include methanol, ethanol, propanol, and butanol. The solvent may comprise a poly-alcohol preferably comprising fewer than 30 carbon atoms, for example fewer than 20 or fewer than 10 carbon atoms. The poly-alcohol preferably comprises more than 2, for example more than 5, or more than 10 hydroxyl groups. Examples of suitable poly-alcohols include ethylene glycol, glycerol, polyethylene glycols, polypropylene glycol and others.

[0064] Preferred formamides include formamide, methyl formamide, dimethyl formamide, and others. Preferred ketones and aldehydes have fewer than 20 carbon atoms, such as fewer than 10 carbon atoms. Exemplary ketones include acetone and methyl ethyl ketone. Exemplary sulfoxides include dimethyl sulfoxide and diethyl sulfoxide.

[0065] The liquid used for cluster formation may comprise a conductivity enhancing compound that enhances the conductivity of the liquid. The conductivity enhancing compound may comprise a preferably volatile salt. For example, an ammonium halide, preferably a quaternium ammonium halide such as an ammonium acetate salt may be used to impart conductivity to the liquid. Other suitable salts include non-volatile alkali metal salts such as NaI, CsI and KI. Preferably, the concentration of salt in the liquid is about 0.1 normal to 2.0 normal.

[0066] In one embodiment of the present invention a surface is impacted with clusters comprising at least one oxidizing agent, which may assist in the chemical removal of targeted material on the substrate surface. Preferably, the amount of oxidizing agent used to prepare the clusters is sufficient to assist the removal process, while being as low as possible to minimize handling, environmental, or similar or related issues, such as cost.

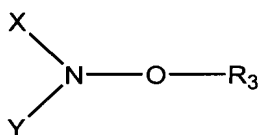
[0067] Clusters comprising an oxidizing agent may be prepared by, for example, a process comprising introducing a liquid comprising one or more oxidizing agents to a cluster generation site. The liquid may be subjected to electrostatic forces sufficient to prepare clusters from the liquid. In one embodiment, the liquid comprises at least 2.5% oxidizing agent, for example, at least 5%, at least 15%, and, in high concentration embodiments, at least 25%, or even at least 35% oxidizing agent. The liquid may comprise 100% or less oxidizing agent, for example less than 75%, or even

less than 50% oxidizing agent. In one embodiment, the liquid consists essentially of the at least one oxidizing agent and one or more solvents, for example, water, alcohol, or poly-alcohol.

[0068] Alternatively, the liquid may comprise other compounds in accordance with the invention including organometallic compounds, corrosion inhibitors and the like.

[0069] An hydroxylamine compound is an exemplary oxidizing agent for use in producing clusters of the present invention. In one embodiment the fluid introduced to the cluster preparation site consists essentially of at least one hydroxylamine compound. In this embodiment, the clusters preferably consist essentially of the at least one hydroxylamine compound. In another embodiment, the fluid introduced to the cluster preparation site comprises at least one hydroxylamine compound and at least one other compound. The at least one other compound may comprise, for example, at least one of (a) one or more solvents and (b) at least one salt. For example, a preferred liquid consists essentially of at least one hydroxylamine compound and at least one solvent.

[0070] The hydroxylamine compound may comprise, for example, at least one of hydroxylamine, a salt of hydroxylamine, a derivative of hydroxylamine, and a salt of a derivative of hydroxylamine. The hydroxylamine compound may be organic or inorganic. Preferably, the hydroxylamine compound satisfies the general formula:



wherein R_3 is hydrogen or a linear, branched, or cyclic hydrocarbon containing from 1 to 7 carbon atoms; and wherein X and Y are, independently, hydrogen or a linear, branched, or cyclic hydrocarbon containing from 1 to 7 carbon atoms, or wherein X and Y are linked together form a nitrogen-containing heterocyclic $\text{C}_4\text{-C}_7$ ring.

[0071] Examples of preferred hydroxylamine compounds according to the invention include hydroxylamine, N-methyl-hydroxylamine, N,N-dimethyl-hydroxylamine, N-ethyl-hydroxylamine, N,N-diethyl-hydroxylamine, methoxylamine, ethoxylamine, N-methyl-methoxylamine, and the like.

[0072] It should be understood that hydroxylamine and its derivatives, as defined above, are available (and may be included in a composition according to the invention) as salts, *e.g.*, sulfate salts, nitrate salts, phosphate salts, or the like, or a combination thereof, and the invention includes these forms of hydroxylamine compounds and their derivatives. In another embodiment, the composition contains hydroxylamine, a sulfate or nitrate salt of hydroxylamine, or a combination

thereof. In some embodiments, the liquid introduced to the cluster generation site is substantially free from hydroxylamine and/or derivatives thereof.

[0073] In one embodiment, the composition according to the invention comprises an amine compound that is not a hydroxyl-containing amine and is not an alkanolamine. Examples of such amine compounds include, but are in no way limited to, o-diaminobenzene, p-diaminobenzene, N-(2-aminoethyl)-ethylenediamine (“AEEDA”), 2-aminoethyl-ethyleneamine, piperazine, N-substituted piperazine derivatives, piperidine, N-substituted piperidine derivatives, diethylene triamine, 2-methyleneaminopropylenediamine, hexamethylene tetramine, and the like, or a combination thereof.

[0074] Preferably the only oxidizing agent in the first liquid composition is an hydroxylamine compound. However, other oxidizing agents can be added or used alternatively.

[0075] The oxidizing agent may comprise an inorganic or organic per-compound. A per-compound is generally defined as a compound containing an element in its highest state of oxidation, such as perchloric acid; or a compound containing at least one peroxy group (--O--O--), such as peracetic acid and perchromic acid. Suitable per-compounds containing at least one peroxy group include, but are not limited to, urea hydrogen peroxide, a monopersulfate, a dipersulfate, peracetic acid, a percarbonate, and an organic peroxide, such as benzoyl peroxide or di-t-butyl peroxide. For example, ozone is a suitable oxidizing agent either alone or in combination with one or more other suitable oxidizing agents.

[0076] One preferred per compound is periodic acid.

[0077] In a preferred per—compound embodiment, the compound containing at least one peroxy group comprises hydrogen peroxide. For example, the liquid introduced to the cluster generation site may consist essentially of hydrogen peroxide or other compound containing at least one peroxy group. Alternatively, the liquid introduced to the cluster generation site comprises a solution of a solvent, such as water, hydrogen peroxide or other compound containing at least one peroxy group. The solution may further include a conductivity enhancing compound. The liquid may consist essentially of the aforementioned solution with or without the conductivity enhancing compound.

[0078] Suitable per-compounds that do not contain a peroxy group include, but are not limited to, periodic acid, any periodate salt, perchloric acid, any perchlorate salt, perbromic acid, and any perbromate salt, perboric acid, and any perborate salt.

[0079] Exemplary oxidizing agents include peroxymonosulfuric acid, potassium peroxymonosulfate, and ammonium peroxymonosulfate.

[0080] Other oxidizing agents are also suitable components of the composition of the present invention. Iodates are useful oxidizers. Oxone is a useful oxidizer.

[0081] The oxidizing agent may be a salt of a metal having multiple oxidation states, a complex or coordination compound of a metal having multiple oxidation states, or any combination thereof, provided the compound has a sufficient oxidative potential to oxidize the substrate. In general, the metal-containing oxidizers are less preferred. Examples include permanganate or salts thereof and perchromate or salts thereof, iron salts, aluminum salts, cerium salts, and the like. When admixed with another common oxidizer such as hydrogen peroxide in a solution, the salts and oxidizer react and the oxidizing capacity of the mixture may decline with time. The nature of the reaction is not known, although it is known that if the pH is above about 5, iron precipitates as $\text{Fe}(\text{OH})_3$ and catalytically decomposes the hydrogen peroxide to oxygen.

[0082] One disadvantage with metal-containing oxidizer salts is that they can leave metal contamination on the substrate. This metallic contamination can result in shorts and spurious conductive properties, along with other problems. Certain metals, such as those with a tendency to plate on or be absorbed on to at least one part of the substrate, may be more damaging than other metals. In one embodiment, the total weight of the metal present in the liquid used to make the clusters is less than 1 percent, less than 0.5 percent, less than 0.2 percent, less than 0.05 percent, less than 0.02 percent or less than 0.005 percent relative to the weight of the liquid. Clusters of the invention may be essentially free of metals, for example, completely free of metals. By essentially free of metals it is meant that the total weight of metal present in the liquid used to generate the clusters is less than 0.25 percent relative to the weight of the liquid. An exception to this preference are embodiments in which the clusters comprise one or more organometallic compounds, which embodiments are discussed elsewhere herein.

[0083] In one embodiment of the present invention, the liquid introduced to the cluster generation site comprises a reducing agent. Hydrazine and/or a derivative of hydrazine are preferred reducing agents. For example, the liquid may comprise an aqueous hydrazine solution. The solution may comprise at least 10% hydrazine, for example, at least 25% hydrazine. The solution preferably includes at least 90% water, for example, at least 65% water. Of course, other hydrazine compatible solvents may be used in place of or in addition to water.

[0084] In another embodiment of the present invention, the liquid introduced to the cluster generation site comprises at least one corrosion inhibitor. Examples of corrosion inhibitors include, but are not limited to, nitrate salts of ammonium; hydrocarbon-substituted ammonium nitrate salts; catechol; benzotriazole; 2,4-pentandione dioxime; 1,6-dioxaspiro[4,4] nonane 2,7-dione (di-ether);

thiourea; ammonium bisulfite; choline bisulfite; choline hydroxide; bischoline hydroxide; trischoline hydroxide; glycerol; sorbitol; gelatine; starch; phosphoric acid; silicic acid; polyethylene oxide; polyethylene imine; and the like; or a combination thereof. Other corrosion inhibitors include choline hydroxide, bischoline hydroxide, or trischoline hydroxide. Preferably, the corrosion inhibitors are substantially free of metals and/or metal ions. Preferred corrosion inhibitors have boiling points in excess of 150 °C, in excess of 200 °C, or in excess of 250 °C.

[0085] In one embodiment, the liquid introduced to the cluster generation site comprises at least one metal, preferably at least one organometallic compound. The liquid may comprise at least one solvent and/or at least one other compound in accordance with the present invention. In one embodiment, the liquid introduced to the cluster generation site consists essentially of at least one organometallic compound and at least one solvent.

[0086] The at least one organometallic compound is preferably a compound comprising at least one metal linked or otherwise associated with carbon. For example, as used herein, the term organometallic compound includes compounds having a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a metal of a main group, transition, lanthanide, or actinide. The metal may be in the form of, for example, an atom or ion. Organic derivatives of the metalloids (e.g. boron, silicon, germanium, arsenic, and tellurium) are considered to be organometallic compounds. Compounds such as molecular metal hydrides, metal alkoxides, thiolates, amides, phosphides, metal complexes containing organo-group 15 and 16 ligands, and metal nitrosyls are also considered to be organometallic compounds.

[0087] With the aid of FIG. 2, the process of generating a beam of clusters will now be described.

The fluid from reservoir 18 flows through the fluid conduit 20 and is delivered to the emitter 32, which is preferably exposed to high vacuum. When the fluid reaches the capillary tip 33, it enters an intense electrostatic field region 37 formed by applying high voltage to the emitter 32. A cluster generation site preferably includes a liquid introduction device, such as the opening of a capillary, by which liquid may be introduced into a region having a pressure of less than about 750 torr, such as less than about 100 torr, such as less than about 10^{-3} torr. The emitter 32 exposed to high vacuum and allowing fluid to be introduced to electrostatic field region 37 is an example of a cluster generation site.

[0088] The preferred voltage is in the range +8 to +20 kV and may be applied using a power supply 17. The electric field 37 is established between the capillary tip 33 and an extractor electrode 30 whose potential is adjustable by means of a power supply 19. The relatively intense fields

generated at the capillary tip 33 ($> 10^5$ volts/cm) result in electrostatic forces stressing the exposed surface of the fluid. As the voltage applied to the emitter 32 is increased, the electrostatic force acting on the fluid surface at the tip 33 also increases until a value is reached that exceeds the surface tension force S holding the fluid together. The fluid disrupts into an aggregate of preferably charged clusters forming a beam of clusters 34 comprising a plurality of clusters. If a positive high voltage is applied to the emitter 32 by means of power supply 17, clusters in a beam 34 will be positively charged. Alternatively, if a negative high voltage is applied to the emitter, the beam 34 will consist of negatively charged clusters.

[0089] Clusters with smaller or larger average diameters can be generated by varying the magnitude of the electric field 37. In general, small clusters, having high charge-to-mass ratios, are generated by high electric fields while large clusters, having lower charge-to-mass ratios, are formed at relatively lower electric fields. When a fixed voltage is applied to the emitter 32, the electric field 37 will increase or decrease depending on the voltage applied to the extraction electrode 30. Conversely, by applying a fixed voltage to the extractor electrode 30, the electric field 37 will increase or decrease depending on the voltage applied to the emitter 32.

[0090] The energy with which clusters impact a target substrate 38 is determined by the voltage applied to the emitter 32, independent of the voltage applied to the extractor electrode 30. In the preferred embodiment of the invention, it is desirable to keep the voltage applied to the emitter constant, corresponding to impact energies greater than 0.5 MeV, and vary the extractor electrode voltage to generate clusters with sizes that efficiently remove contaminants. In summary, the voltage applied to the capillary emitter can be used to control the cluster impact energy and the voltage applied to the extractor electrode can be used to control the mean cluster size.

[0091] It should be pointed out that the cluster size distribution in the beam 34 can be modified by other means when the electric field 37 is fixed by the voltages applied to the emitter 32 and the extractor electrode 30. Mean cluster sizes in the distribution can also be shifted to yield smaller or larger mean cluster diameters by varying the flow rate of the conductive fluid, with low flow rates corresponding to smaller clusters and high flow rates corresponding to larger clusters. Finally, for a given fluid flow rate and voltage applied to the emitter 32 and extractor electrode 30, the mean cluster size characterizing the distribution can be modified by varying the conductivity of the fluid 21. For the purpose of removing micron and submicron particulates from wafer surfaces, clusters with mean diameters in the range 0.01-0.05 micron are preferred. From the foregoing discussion, it is apparent that the system provides sufficient flexibility to adjust the process variables for producing

clusters with desired sizes and energies to efficiently remove particulate or organic film contaminants from surfaces.

[0092] The cluster beam 34, formed by electrostatically dispersing the fluid at the capillary tip 33, is accelerated by the electric field 37 existing in the gap separating the emitter 32 from the extractor electrode 30. In a preferred embodiment of the invention, a circular opening or extractor aperture 35 in the extractor electrode 30 has a diameter whose dimensions are on the order of 0.3 to 0.95 cm. For symmetry considerations, the extractor aperture 35 is usually circular, if the emitter 32 is tubular, but it is possible to use other shapes. The preferred alignment of the emitter-extractor electrode combination consists of placing the emitter 32 coaxially at the center of the extractor aperture 35 such that the capillary tip 33 lies in the mid-plane of the extractor electrode 30. Although this arrangement is preferred, satisfactory operation can be achieved if the capillary tip 33 is positioned directly behind the rear surface of the extractor electrode 30 to a distance of 0.3 cm. Further retraction of the emitter 32 can cause excessive impingement of the cluster beam 34 on the backside of the extractor electrode 30. Bombardment of the extractor electrode 30 by charged clusters in the beam eject secondary electrons that are accelerated back to the capillary tip 33 causing uncontrolled tip heating when a positive high voltage is applied to the emitter 32.

[0093] As seen in FIG. 1, the cluster beam 34 formation and acceleration process is preferably carried out in a vacuum chamber 27. A stationary or transportable target substrate 38 is interposed in the cluster beam 34. In a preferred embodiment of the invention, a non-focused, divergent cluster beam impacts the target substrate 38. In this manner, a large area of the substrate can be impacted as opposed to a smaller area impacted by a focused beam. Individual clusters in the beam impact the surface of the target substrate 38 resulting in the effective removal of various types of contaminants. In some instances and for efficacious removal of contaminants, it is desirable to rotate the target substrate 38 with respect to the cluster beam 34 allowing impacts to occur at acute angles of incidence. Contaminants driven from the target substrate 38 may deposit on the surfaces of a cryogenic collector 36, cooled by liquid nitrogen or other means preventing their re-deposition on the cleansed substrate surface. An alternate impaction or collection surface may consist of an uncoated, porous, sintered metal mesh or a teflon membrane filter. Particulates removed from surfaces by the impact of cluster beams provide an extremely light loading on collection surfaces. In view of the loading conditions, an oil-coated teflon membrane filter can provide a surface with a collection efficiency of 100% as discussed by C. Tsai, "Solid Particle Collection Characteristics on Impaction Surfaces of Different Designs", *Aerosol Sci. Technol.*, 23, 96, 1995. An oil for applying a thin coating to collection surfaces is preferably one having an extremely low vapor pressure about

10^{-10} torr) e.g., a silicone diffusion pump fluid, Model D-7050, manufactured by Dow Corning. Metal or dielectric surfaces charged by application of voltages can suffice for collecting ejected particulate contaminants in some applications.

[0094] Several properties of the cluster impacts are important and relevant to the processes of contaminant removal and deposition. Cluster velocities may be supersonic and, depending on the acceleration voltage applied to the emitter 32, can exceed the velocity of sound in the impacted material. It is believed that shock waves can be induced in the material impacted (substrate 38, films or particulates) causing shock unloading or liftoff of contaminant species. Because individual clusters can carry a large number of charges ($N > 100$), clusters accelerated through 10 kV or more have impact energies of the order 0.5 to 2.0 MeV's which are deposited over an extended area of the target substrate 38. The direct transfer of a portion of this collisional energy can overcome London - Van der Waals and electrostatic forces bonding contaminants to surfaces.

[0095] The massiveness of individual clusters in the beam 34, preferably on the order of 10^{-17} to 10^{-16} grams, in combination with their supersonic velocities, provides a means for transferring a large momentum to film and particulate contaminants, especially for events involving multiple and energetically additive collisions.

[0096] A unique feature of the present invention is that, compared to atomic ion or small molecular ion beams, the massiveness of the clusters employed here for cleaning contaminated surfaces insures that the total cluster energy is shared by the large number of nucleons comprising the clusters. Although the total cluster energy may exceed 1 MeV, individual nucleons which participate in collisions have specific energies less than 1 eV/nucleon. On the atomic level, damage or sputtering of the target substrate is prevented. In the preferred embodiment of the invention, this is a critical feature since contaminants must be removed without causing substrate damage or removal of permanent features essential for operating devices constructed from the substrate material. Another unique feature of the present invention is that beam clusters are comparable in size to individual particulate contaminants with diameters less than 1 micron. Submicron clusters are particularly effective for interacting with and removing particulates less than 0.1 micron, a particularly troublesome size if future microelectronics devices are to provide features with sizes approaching 0.07 micron.

[0097] In some embodiments of the present invention it is desired to deposit at least some material present in the clusters upon the impacted surface. For example, as discussed above, clusters comprising one or more corrosion inhibitors may be impacted upon a surface. In another embodiment, clusters comprising one or more metals, such as one or more organometallic

compounds are impacted upon a surface. When depositing material upon a surface it is preferred to reduce the average kinetic energy of the clusters with respect to the average kinetic energy of clusters used to remove contaminants. For example, in preferred embodiments clusters having energies of less than about 1.5 MeV, for example, less than 0.75 MeV, less than 0.5 MeV, or even less than 0.4 MeV may be used to deposit material upon a surface.

[0098] In one embodiment, of the present invention the surface is subjected to impact with clusters prepared from a first liquid. The surface is also subjected to impact with clusters prepared from a second liquid, which may be different from the first liquid. For example, the second liquid may include a different solvent and/or solute from the first liquid. In a preferred embodiment, clusters prepared from the first liquid remove particulates or other contaminants from the surface. It is preferred that material present in clusters prepared from the first liquid essentially does not deposit upon the surface. Material present in clusters prepared from the second liquid, however, may be desirably deposited upon at least a portion of the surface. Such deposited material may include at least one of corrosion inhibitors and compounds comprising a metal.

[0099] In deposition mode, clusters having a lower kinetic energy may be prepared by reducing the absolute electrical potential of the emitter as compared to the absolute electrical potential of the emitter when clusters are prepared to remove contaminants. The potential of the emitter may be determined relative to the potential of the surface to be impacted. In one embodiment, for example, a first plurality of clusters is impacted upon a surface to remove contaminants therefrom. A second plurality of clusters may then be impacted upon at least a portion of the surface to deposit at least some material present in clusters of the second plurality of clusters upon the surface. Clusters of the second plurality of clusters may have kinetic energies at least 10% less, at least 25% less, or at least 50% less than clusters of the first plurality of clusters.

[00100] In a preferred embodiment, the step of impacting the surface with clusters prepared from the second liquid occurs after the step of impacting with surface with clusters prepared from the first liquid has been initiated. A given area of the surface may first be subjected to impact with clusters prepared from the first liquid and then subjected to impact with clusters prepared from the second liquid. If the step of impacting with clusters prepared from the second liquid is performed subsequent to the step of impacting with clusters prepared from the first liquid, it is preferred that the surface not be exposed to environments comprising excessive number of particulates in between performing the two steps. For example, the surface is preferably not exposed to environments comprising more than 1000 particulates of a diameter exceeding 0.5 microns per square foot of atmosphere in between the two steps. More preferably, the surface is preferably not exposed to

environments comprising more than 100 particulates of a diameter exceeding 0.5 microns per square foot of atmosphere in between the two steps. The term particulates, as used in this context, does not include clusters prepared in accordance with the present invention.

[00101] During the steps of impacting with the first and second liquids, the surface is preferably exposed to a pressure of less than 500 torr, for example less than 100 torr or even less than 10 torr. If the step of impacting with clusters prepared from the second liquid is performed subsequent to the step of impacting with clusters prepared from the first liquid, it is preferred that the surface not be exposed to a pressure of greater than 500 torr, 100 torr, or 10 torr in between performing the two steps.

[00102] If means are not provided for bleeding off excess charge buildup on the target substrate 38, surface charging can occur in the presence of the cluster beam 34. The buildup of potential by surface charging can lead to beam deceleration, reducing the impact energy of the clusters. Further, variations in the potentials between neighboring regions on the target substrate 38 can promote local discharging causing damage to substrate features. In the present embodiment of the invention, a neutralization method is employed to prevent charging of the substrate exposed to a positively charged cluster beam. Referring to FIG. 2, a thermionic emitter 44, preferably made from tantalum or other refractory material which emits copious electrons on being heated, is positioned below the extractor electrode 30. The thermionic emitter 44 is preferably constructed from small diameter wire, in the range 0.010 to 0.020 inches, and bent in a circle symmetrically positioned on the longitudinal axis of the tubular capillary emitter 32. The thermionic emitter 44 can be heated by means of a filament power supply 46 and biased a few volts negative by means of a power supply 48 which provides the energy necessary to launch the electrons along trajectories 42. Electrons escaping the thermionic emitter 44 leave by way of a circular opening placed in the neutralizer shield 40.

Neutralization of the cluster beam can be accomplished by trapping electrons within the beam and by the capture of electrons by individual, positively charged clusters. Alternative means for injecting electrons into a beam for neutralization exist with different configurations and materials and need not be discussed here without departing from the scope or spirit of the present invention.

[00103] In order to provide multiple cluster beams for impacting and cleaning larger surface areas and for decreasing the time required to remove contaminants, a second embodiment of the processing apparatus will now be described. FIG. 3 illustrates a linear array consisting of a plurality of emitters 32 for generating multiple, cluster beams. When a plurality of emitters form an array that is linear, hexagonally packed or configured to some other suitable geometry, a single extractor electrode 30 having multiple, circular apertures 35 may be used. The multiaperture extractor

electrode provides the geometry required to establish the intense electric fields at each of the capillary emitters comprising the array. Neutralization of the multiple beams can be provided by a single thermionic emitter 44 described previously for use with a single capillary emitter, configured to conform to the linear dimensions of the array. Positive high voltage in the range +8 to +20 kV, preferably +15 kV in the present embodiment, is applied to each of the capillary emitters by means of a power supply 17. The individual emitters comprising the array can be wired in parallel as shown in FIG. 3.

[00104] As an alternate to using a plurality of emitters 32, a linear capillary slit 62 as shown in FIG. 5 may be provided. By applying voltage to the capillary slit, a plurality of emissive sites will be formed in the fluid along the slit edges, resulting in the production of plural beams of clusters. The preferred width of the slit channel 64 filled with fluid 21 is of the order 0.001 to 0.004 inches. In FIG. 5 a slotted extractor electrode 60 aids in establishing the intense electric field at the slit edges. Beam neutralization for this configuration (not shown) can be provided by an electron emitting wire filament as seen in FIG. 3.

[00105] With the aid of FIG. 4, a novel means for providing beam neutralization is accomplished by employing two or more linear arrays. The left side of FIG. 4 illustrates a linear array consisting of a plurality of capillary emitters 32 wired in parallel to a power supply 17. Positively charged cluster beams will be generated by the array when positive high voltage is applied by means of power supply 17. Similarly, the right side of FIG. 4 illustrates an adjacent linear array consisting of a plurality of capillary emitters 32 wired in parallel to power supply 23. Negatively charged cluster beams will be formed by the array when negative voltage is applied by means of a power supply 23. Using this bipolar arrangement, beams consisting of positively and negatively charged clusters can be generated simultaneously. Beam neutralization can be achieved by adjusting the positive and negative voltages applied by power supplies 17 and 23 until the net charge buildup on the target substrate 38 is approximately zero.

[00106] An alternate embodiment of the invention allows for an ion optical system capable of focusing and deflecting the cluster beam. By positioning the beam at precise locations on a target substrate, contaminants can be removed from a first portion of the surface with subjecting a second portion of the surface to impaction with clusters. FIG. 6 shows a three-element electrostatic lens 50 used to focus the cluster beam 34 generated by an emitter 32. In this arrangement, a focusing voltage is applied to the mid- element lens plate by means of a power supply 52. The polarity of the applied voltage will depend on whether a positive or negative cluster beam is formed. Although FIG. 6 shows a symmetrical, Einzel aperture type lens, other types and geometries of electrostatic

lenses can be used to control cluster beams without departing from the scope or spirit of the present invention. These include slit, tubular cylinders and geometrically asymmetric lenses. Electrostatic deflection and rastering to precisely position the cluster beam on the substrate 38 can be provided by a set of orthogonal deflector plates 56, 58 - controlled by applying variable or fixed voltages by means of a rastering power supply 54.

[00107] A focused or deflected cluster beam may be used to deposit material upon only selected portions of a surface leaving little or no material deposited upon other portions of the surface. For example, in one embodiment of the invention, a first portion of a surface is subjected to impact with clusters of a first plurality of clusters to remove contaminants from the surface or otherwise prepare the surface for deposition of a material, for example, a corrosion inhibitor or metal. A second portion of the surface is impacted with clusters of a focused second plurality clusters, the clusters comprising a material to be deposited upon the second portion of the surface. The second portion of the surface preferably comprises a subset of the first portion of the surface. For example, the second portion of the surface may comprise a network of one or more electrical connections.

[00108] The foregoing description of the preferred embodiment of the invention has been presented for the purposes of illustration and description. However, the foregoing description is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many changes and modifications may be made to the invention by one having ordinary skill in the art, without departing from the spirit or scope of the invention.